Molecular dynamics of a dense fluid of polydisperse hard spheres

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Abstract

Slow dynamics in a fluid are studied in one of the most basic systems possible: polydisperse hard spheres. Monodisperse hard spheres cannot be studied as the slow down in dynamics as the density is increased is preempted by crystallisation. As the dynamics slow they become more heterogeneous, the spread in the distances traveled by different particles in the same time increases. However, the dynamics appears to be less heterogeneous than in hard-sphere-like colloids at the same volume fraction. The particles which move least far in a characteristic relaxation time and, particularly, the particles which move farthest in the same time are clustered, not randomly distributed throughout the sample. We study the dynamics at three different widths of the distribution of diameters of the hard spheres. For each width, the relaxation time is the same function of the compressibility factor, suggesting that this determines the relaxation time for hard spheres.

1 Introduction

The study of hard spheres has taught us much about the equilibrium and dynamic behaviour of dense fluids and crystals. We have learnt that crystallisation can be a result of the more efficient packing in the crystal of atoms or colloids, and that diffusion is inhibited in dense fluids by repeated collisions of particles with their neighbours. One outstanding problem is that of understanding and perhaps trying to predict, the dramatic slowdown of the dynamics of fluids and the formation of a glass; see Refs. 1–3 for introductions to slow dynamics and glasses. An obvious thing to do is to study this phenomenon in hard spheres. This has been done and the results are presented here.

Unfortunately, monodisperse hard spheres crystallise readily, preventing the study of hard spheres at densities high enough to observe very slow dynamics. Crystallisation is inhibited if the spheres are not all the same size. Speedy studied a binary mixture of hard spheres of two diameters,[4] which did not crystallise. Here mixtures of spheres with continuous ranges of diameters are studied, these are called polydisperse mixtures. This will enable us to compare with experiments on hard-sphere colloids, which are inevitably on polydisperse particles,.[5–7] Monte Carlo simulations of polydisperse hard spheres have been performed by Doliwa and Heuer.[8, 9]

In this contribution we will quantify the slow down in the dynamics, characterise these slow dynamics, and assess the effect of having spheres of different diameters present. The slow down is measured by calculating a relaxation time. The dynamics are characterised by calculating their deviation from what we would expect if each particle was diffusing independently. When the deviations are large we call the dynamics heterogeneous. When the dynamics are heterogeneous, the distribution of speeds and relaxation times of individual particles is much broader than the Gaussian function obtained when particles are diffusing independently. There are many more particles which have traveled much farther than the mean than we would expect for independent diffusion of each particle. These fast-moving particles are not distributed randomly in space, they are concentrated in clusters. In other words, fast particles tend to be surrounded by other fast particles.[10–13]

Three different widths of the distribution of diameters are studied. The polydispersity width is characterised by the standard deviation of the distribution in diameters. For the three distributions this is 9, 14 and 20%. As in experiments on hard-sphere colloids[14, 15] if the distribution is narrower the spheres can crystallise. Surprisingly, although increasing the polydispersity at fixed volume fraction speeds up relaxation, the relaxation time is, within simulation resolution, independent of the width of the distribution at fixed compressibility factor. The relaxation time appears to depend only on the compressibility factor. We also study the effect of the heterogeneity in diameters on the heterogeneity in the dynamics.

In the next section we briefly describe our, standard, methodology. Section 3 outlines when our simulations crystallised and quantifies how much polydispersity in the diameters is required to avoid crystallisation. Section 4 discusses a thermodynamic property, the pressure. The last but one section contains our results for the dynamics, and the last section is a discussion. All results are for fluids at

equilibrium not glasses. The focus is on the relaxation of the structure of the fluids, diffusion coefficients and other properties of motion at times large with respect to the relaxation time are not calculated.

2 Simulation methodology

Conventional NpT Monte Carlo and NVE molecular dynamics techniques are used.[16] N, p, V, E, and T are the number of particles, the pressure, the volume, the energy and the temperature, respectively. The only nonstandard part concerns the polydispersity of the system, the presence of spheres of different diameters. In theoretical treatments of polydispersity first the thermodynamic limit $N \to \infty$, is taken and then the number of components present is taken to ∞. This gives rise to a continuous distribution of sizes of spheres[17,18] with a number density $\rho x(\sigma)d\sigma$ of spheres in the range σ to $\sigma + d\sigma$. $\rho = N/V$ is the total number density of spheres. The width of the distribution of diameters can be characterised by a (dimensionless) width parameter w. The larger w is the broader the distribution of sizes present in the mixture. In the limit $w \to 0$ we recover a monodisperse system. A simple functional form for the distribution function x is the hat function:

$$x(\sigma) = \begin{cases} 0 & \sigma < \overline{\sigma}(1 - w/2) \\ (\overline{\sigma}w)^{-1} & \overline{\sigma}(1 - w/2) \leq \sigma \leq \overline{\sigma}(1 + w/2) \\ 0 & \sigma > \overline{\sigma}(1 + w/2) \end{cases} , \tag{1}$$

where $\overline{\sigma}$ is the mean diameter. The standard deviation divided by its mean, of the distribution $x(\sigma)$, $s = w/\sqrt{12}$.

Simulations are of course of a finite system — we cannot take the thermodynamic limit in a simulation. For finite N, $x(\sigma)$ cannot be a continuous function. For our simulations we generate a set of N diameters by generating a set of N pseudo-random numbers in the range $\overline{\sigma}(1 - w/2)$ to $\overline{\sigma}(1 + w/2)$. Ideally we would average over many different realisations of the polydispersity by performing computer simulations for many different sets of the N diameters. However, as our systems have long relaxation times and so require long runs this is not feasible. Thus all the results we will present for a given polydispersity width will be for a single system of 1372 particles with one set of the 1372 diameters. We have performed some simulations with different sets of the diameters but the same number of particles and the results did not change significantly. We have also performed simulations with 256 and 500 particles and obtained results which did not differ significantly with the exception of some results for the dynamics. We discuss these differences below.

NpT Monte Carlo simulations are used to start with and to compress the fluid phase up to the required density. NVE molecular dynamics are used to equilibrate at a particular density and to obtain all the averages shown, including the pressure. All simulation results are for fluids at (possibly metastable) equilibrium, not for glasses. Our results are in reduced units. We use the mean diameter $\overline{\sigma}$ as our length scale. The reduced pressure p_r is then $p_r = Z\rho\overline{\sigma}^3$, where ρ is the number density of particles and $Z = pV/(NkT)$ is the compressibility factor. The results are all averages over 8 runs. We use the variation between the results of the individual runs to estimate statistical errors. In no case are they significantly larger than the plot symbols used in the figures.

A time scale can obtained by the ratio of a distance to a velocity. The velocity we choose is the root mean square velocity along one of the 3 Cartesian axes, of a particle with a diameter equal to the mean diameter. This velocity is equal to $(kT/\overline{m})^{1/2}$, where $\overline{m}$ is the mass of particle with diameter $\overline{\sigma}$. The time scale is thus $\overline{\sigma}(\overline{m}/kT)^{1/2}$ and all times will be made dimensionless by dividing by this. For molecular dynamics we have to specify the masses of the particles. We assume that the mass of a sphere scales with the cube of its radius, correct if all spheres are made from the same substance with the same uniform density. The density we use is the volume fraction $\eta = (\pi/6)\rho\overline{\sigma^3}$, where $\overline{\sigma^3}$ is the third moment of $x(\sigma)$.

3 Crystallisation

Although we will present results only for systems which showed no sign of crystallising, some of our systems did start to crystallise. Speedy[19] has undertaken a study of the freezing of monodisperse hard spheres within molecular dynamics simulations. He finds crystallisation only above a volume fraction of 0.54. We simulated 1372 monodisperse hard spheres. They were stable for a time much longer than the relaxation time of the fluid at a volume fraction $\eta = 0.54$ but crystallised at $\eta = 0.56$. Thus we agree with the findings of Speedy. Simulations of 1372 spheres with a polydispersity width of $w = 0.1$ also crystallised but when the width was increased to $w = 0.2$ ($s = 5.8\%$) the fluid was stable, it never crystallised. Simulations at polydispersity widths $w = 0.3$, 0.5 and 0.7, of both 256 and 1372 spheres, never showed any sign of crystallisation. They remained amorphous up to the highest densities simulated. Widths $w = 0.3$, 0.5 and 0.7 correspond to values of s of 8.7%, 14.4% and 20.2%, respectively.

Experiments on colloids find no crystallisation for polydispersities beyond a standard deviation s close to 8%.[14,15] Thus our finding of crystallisation when the standard deviation is 3% ($w = 0.1$) but not when it is 6% ($w = 0.2$) is consistent with experiment. However, our simulations are for systems much much smaller than experiment and the time elapsed until nucleation occurs will depend on system size. Theoretical and computer simulation studies of the equilibrium phase behaviour of polydisperse hard spheres[20–27] show that polydispersity destabilises the crystalline phase, pushing the fluid-crystal transition to higher volume fractions.

Our systems with polydispersity widths of $w = 0.2$, 0.3, 0.5 and 0.7 do not crystallise even at volume fractions up

to 0.58 because either the fluid phase is still the equilibrium phase even at these high densities or it is metastable with respect to fluid-crystal coexistence but the fluid is not sufficiently deep into the coexistence region for the barrier to nucleation of the crystalline phase to be small.[3] The nucleation rate varies as the inverse of the product of the relaxation time and the exponential of the free energy barrier.[3] If the barrier is large up to densities at which the relaxation time is very large, say $\eta = 0.57$-0.58, then the rate will always be very small. Perhaps too small to be observed.

Theoretical studies[20–22,25,26] suggest that for polydispersity widths of around 0.3 and greater, the crystalline phase cannot form with the full width of the distribution. It can only form if it accepts only a narrow range of diameters. Neither in experiments[14,15] nor here is the formation of a crystalline phase with a narrow range of diameters observed to form from a polydisperse mixture of spheres. It is not clear whether or not the fact that the crystalline phase can only form from a fraction of the distribution of diameters is a cause of the fact that crystallisation is not observed.

We checked for segregation of the large and small spheres, i.e., for a tendency to phase separate into a phase of large spheres coexisting with a phase of small spheres. There was no sign of such segregation. Segregation is not expected at the polydispersity widths studied here in the fluid phase. The Boublik-Mansoori-Carnahan-Starling-Leland (BMCSL) theory[28,29] as generalised to polydisperse hard spheres by Salacuse and Stell[17] does however predict phase separation at much broader distributions of diameters.[30,31] This fluid-fluid separation is metastable with respect to phase separation plus crystallisation of the large spheres.[32]

4 Pressure

The reduced pressure is plotted as a function of volume fraction in Fig. 1. Results from simulation are shown along with the predictions of the BMCSL expression for the pressure.[17,28,29] The agreement between the BMCSL equation and simulation is excellent. The only noticeable deviation is that the BMCSL is a little too high at the highest densities for $w = 0.3$ and 0.5.

The pressure tends to decrease as the polydispersity width increases. The random-close-packing density of polydisperse hard spheres increases as the polydispersity width increases.[33,34] The pressure diverges at random-close-packing. Therefore, at constant η we move farther from the density where the pressure diverges as the polydispersity width increases and so it is unsurprising that the pressure decreases. The distribution used in Refs. 33,34 was different to the hat function used here but the trend should be relatively insensitive to the exact form of the distribution when the polydispersity is not too great.

5 Dynamics

As we are considering dense states the motion of a particle is strongly restricted by its neighbours. Over some timescale a particle will rattle back and fore in a cage formed by its neighbours; then as we are considering a fluid not a glass, the particle will 'break out' of the cage and eventually its motion will be diffusive. We can assess whether or not particles are just rattling back and fore or are moving significant distances, i.e., distances comparable to their own diameter, by examining the intermediate scattering function, sometimes called the self incoherent intermediate scattering function, $F_s(q,t)$. As indicated it is a function of wavevector q and time t, it is also a function of volume fraction and polydispersity. It is defined by[35]

$$F_s(q,t) = \frac{1}{N} \sum_{i=1}^{N} \cos(\mathbf{q}.[\mathbf{r}_i(t) - \mathbf{r}_i(0)]), \qquad (2)$$

where $\mathbf{r}_i(t)$ is the position vector for the ith particle at time t. For the fluids we consider, it is not a function of the initial time, taken to be $t = 0$ above, only of the time elapsed, t. For our isotropic systems it is also only a function of the magnitude q of the wavevector $\mathbf{q}$, not of its orientation. To improve statistics we average over wavevectors along the x, y and z axes. Clearly $F_s(q,0) = 1$ and at times t sufficiently long that the positions of the particles are no longer correlated with their positions at time $t = 0$, then $F_s(q,t) = 0$. As the particles move, their positions become decorrelated with their positions at $t = 0$ and F_s decays to 0. For a fixed q, $F_s(q,t)$ will become small when the particles have moved a distance of about $\pi/(2q)$. All our results are for $q = 2\pi/\overline{\sigma}$, and so F_s will become small when most of the particles have moved a distance of around a quarter of their diameter. F_s enables us to define a relaxation or correlation time for the dynamics, τ. We define τ by

$$F_s(2\pi/\overline{\sigma}, \tau) = 1/e. \qquad (3)$$

Values of τ for $w = 0.3$, 0.5 and 0.7 are shown in Fig. 2. As expected τ increases rapidly as the volume fraction increases; by about 2 orders of magnitude between $\eta = 0.5$ and 0.58. It is also clear that at constant volume fraction, increasing the polydispersity decreases the relaxation time τ. However, if the relaxation time is plotted as a function of the compressibility factor Z, Fig. 3, then the data for the 3 polydispersity widths essentially follow the same curve. Note that in Fig. 3 we have included data for monodisperse spheres (at densities below where they crystallise) and shown results down to $\eta = 0.3$. Spheres with a polydispersity width of $w = 0.7$ at $\eta = 0.57$ have almost the same Z and almost the same relaxation time as spheres with $w = 0.3$ at $\eta = 0.56$. These are the two points which are almost superposed in Fig. 3. To a good approximation the relaxation time as defined by Eq. (3) is a function only of the compressibility factor $Z = pV/(NkT)$. It is not obvious to the author why τ should depend only on Z although there are theories which attempt to relate dynamic

quantities such as τ to thermodynamic quantities.[1,3] If we plot τ as a function of the reduced pressure p_r (not shown) then the results for the 3 polydispersity widths do not fall on the same curve, in particular the results for $w = 0.7$ are above those for the narrower distributions.

We should note that for $\eta = 0.56$ and above the relaxation times calculated using 256 spheres are consistently above those calculated with 1372 spheres. For $w = 0.3$ and $\eta = 0.57$ the relaxation times are 77 and 110 for 1372 and 256 spheres, respectively. This suggests that the result for 1372 spheres is 10-30% higher than that of an infinite system. When τ is large, we observe finite size effects for the dynamics but not for the statics. This seems to be a quite general finding.[36] It suggests that there is some length scale associated with the dynamics but not the statics which grows as the relaxation time τ increases. Recently this possibility has been extensively studied by Glotzer and coworkers.[12,13,37,38] They define a purely dynamical correlation length and observe that it increases as the dynamics slow down. Perhaps the easiest way to see the correlations in the dynamics is to plot out the fastest and slowest moving particles. We simulate the particles with $w = 0.3$ at the highest volume fraction studied for this polydispersity, $\eta = 0.57$. Fig. 4 shows the fastest 5% of the 1372 particles, while Fig. 5 shows the slowest 5%. Fastest and slowest are defined as having the largest or smallest displacement over a time interval of length 29.4. This is a little less than half the relaxation time τ. Clearly, neither the fastest nor the slowest particles are randomly distributed, both show strong clustering — the dynamics are highly correlated. This has been observed in previous simulation studies.[10–13,36–38]

So over times of order τ the positions of the fastest particles are correlated. The movement of the particles is very far from being independent diffusion of each particle. If the particles were diffusing independently then for each particle, the probability of finding the particle at a point would be a Gaussian function of the distance between the point and the position of the particle at $t = 0$. As they are not diffusing independently it will be not be a Gaussian. We can measure deviations of the distribution of particles from a Gaussian by using the non-Gaussian parameter introduced by Rahman[39] and defined by

$$\alpha(t) = \frac{3N^{-1}\sum_{i=1}^{N}[\mathbf{r}_i(t) - \mathbf{r}_i(0)]^4}{5\left(N^{-1}\sum_{i=1}^{N}[\mathbf{r}_i(t) - \mathbf{r}_i(0)]^2\right)^2} - 1. \qquad (4)$$

For a Gaussian distribution the ratio of the fourth moment to the square of the second is 5/3 and $\alpha = 0$. In Fig. 6 we have plotted α as a function of time for a number of volume fractions. For monodisperse particles the Maxwell-Boltzmann distribution of velocities enforces $\alpha = 0$ in the short time, ballistic, regime, and at times much longer than τ we have diffusion and again $\alpha = 0$. For polydisperse particles α is nonzero in the ballistic regime due to different particles having different masses, and nonzero at very long times due to larger particles having smaller diffusion coef-

ficients than smaller particles. So, in Fig. 6 α is always nonzero. The value of α in the ballistic limit depends only on the polydispersity width w, its value in the other limit comes from the spread in diffusion coefficients with particle size and so will also depend on density. Positive values of α come from a large fourth moment, due to more particles with large displacements than would be found for a Gaussian distribution with the same second moment. It is clear if we compare Fig. 6 with the relaxation times of Fig. 2 that the non-Gaussian parameter α goes through a maximum at a time comparable to but (at least at the highest densities) less than the relaxation time τ. This maximum value increases rapidly as τ increases. The deviations from a Gaussian are much larger at a volume fraction of 0.57 than at 0.5.

Recently, experiments have imaged colloidal suspensions of hard-sphere-like particles at the high volume fractions considered here.[5–7] The suspensions are of particles with somewhat smaller polydispersities than considered here, 8%,[5] 6%[6] and 5%.[7] The dynamics of colloidal particles,[40] are rather different from those of free particles such as our hard spheres. Colloidal particles are immersed in fluid and so their motion is diffusive on all time scales on which the particles move a significant distance. In addition, the motion of nearby particles is coupled by hydrodynamic interactions through the fluid. If we compare the α values measured by Weeks et $al.$[7] with those of Fig. 6 we find that the simulation and experimental results are rather different. The experimental values of α are consistently larger than those in Fig. 6, Weeks et $al.$ measure a maximum α at $\eta = 0.52$ of about 1.5 and at $\eta = 0.56$ of a little under 2.5. The dynamics on a time scale of the relaxation time τ must be rather different for colloidal particles and free particles, although in both cases the relaxation time increases very rapidly and in both cases glasses can form. The results of Kegel and van Blaaderen[6] for α are also larger than our simulation results; those of Kasper et $al.$[5] are much larger, at $\eta = 0.56$ the maximum value of α is over 5.

Two obvious sources of the difference between molecular dynamics simulation and experiment are: i) the motion of colloidal particles is diffusive even on time scales much less than τ, and ii) hydrodynamic interactions between particles. i) and ii) could be distinguished by performing both molecular dynamics and Brownian dynamics of the same potential.[41,42] Brownian dynamics is an approximation to the dynamics of particles in a fluid which accounts for the fact that particles diffuse even over very small length scales but neglects hydrodynamic interactions between particles.[40]

Another way to look at the large spread in the amount individual particles are moving is to define F_s's for each particle, and then use this to obtain a relaxation time for each particle. Averaging over wavevectors along the x, y and z axes we have for the ith particle

$$\frac{1}{3}\left\{\cos(q[x_i(\zeta_i) - x_i(0)]) + \cos(q[y_i(\zeta_i) - y_i(0)]) +\right.$$

$$\cos(q[z_i(\zeta_i) - z_i(0)])\} = 1/e, \quad (5)$$

which defines the relaxation time for the ith particle, ζ_i. As always $q = 2\pi/\overline{\sigma}$. In Fig. 7 we have plotted the probability function $P(\zeta)$, where $P(\zeta)d\zeta$ is the probability that a particle will have a relaxation time between ζ and $\zeta + d\zeta$. For both $\eta = 0.5$ and 0.56 there is a peak at short times and then P decays. The decay is clearly close to exponential, which makes sense as (at not-too-short times) the probability of a particle leaving its cage in some short time interval should be independent of time; at equilibrium the environment of a particle or cluster of particles is on average not changing with time. For $\eta = 0.5$ the peak is a little below τ at that density but for $\eta = 0.56$ the peak is at about one tenth of τ. At the higher density the probability distribution of ζ is very broad.

5.1 Polydispersity

The spheres are polydisperse, different spheres have different diameters and so their static and dynamic properties will differ. We expect the smaller spheres to move larger distances than larger spheres in the same time. At very short times, in the ballistic regime, this is trivially true due to the smaller mass and hence higher velocity of the smaller spheres. We can look at motion over a time scale of order τ by examining the sizes of the fastest and slowest 5% of the spheres. Figs. 4 and 5 show these spheres for $w = 0.3$. We average over 8 runs with an average time interval close to that in Figs. 4 and 5. The average diameter of the fastest 5% (69) of the spheres, over a time interval of 29.2, is $0.95\overline{\sigma} \pm 0.01\overline{\sigma}$, and for the slowest 5% it is $1.01\overline{\sigma} \pm 0.01\overline{\sigma}$. The effect is small but as we would expect the fastest spheres are smaller than average. For a polydispersity width of 0.7, over a time interval of 5.88, the average diameter of the fastest 5% is $0.79\overline{\sigma} \pm 0.02\overline{\sigma}$, and for the slowest 5% it is $1.08 \pm 0.02\overline{\sigma}$. A time of 5.88 is, as with the less polydisperse spheres, somewhat less than half τ and so near the maximum in α. Of course the effect is now larger but still the slowest spheres are not much larger than the mean, their mean diameter would have been above 1.3 if all the slowest spheres were also the largest. The difference between the mean diameter of the fastest spheres and the overall mean diameter is twice the difference between the mean diameter of the slowest spheres and the overall mean diameter.

We have defined an intermediate scattering function, F_s, for all spheres regardless of diameter in Eq. (2). We can also define an intermediate scattering function for subsets of the particles with diameters in some range σ_{min} to σ_{max}, $F_s(q, t; \sigma_{min}, \sigma_{max})$. The definition is completely analogous to that of the total $F_s(q, t)$ in Eq. (2),

$$F_s(q, t; \sigma_{min}, \sigma_{max}) =$$
$$\frac{1}{N_{mm}} \sum_{i=1}^{N_{mm}} \cos(\mathbf{q}.[\mathbf{r}_i(t) - \mathbf{r}_i(0)]),$$
$$(6)$$

where the sum is over all spheres with diameters in the range σ_{min} to σ_{max}, and N_{mm} is the number of spheres in this range. As before $q = 2\pi/\overline{\sigma}$ and we average over wavevectors along the x, y and z axes. We will study intermediate scattering functions for the smallest, $F_s^{(s)}(q, t)$, and largest spheres, $F_s^{(l)}(q, t)$, defined by

$$
\begin{aligned}
F_s^{(s)}(q, t) &= F_s(q, t; \overline{\sigma}(1 - w/2), \overline{\sigma}(1 - w/2 + 0.05)) \\
F_s^{(l)}(q, t) &= F_s(q, t; \overline{\sigma}(1 + w/2 - 0.05), \overline{\sigma}(1 + w/2)).
\end{aligned}
$$
$$(7)$$

These are for the particles within $0.05\overline{\sigma}$ of the minimum or maximum diameter. For $w = 0.7$ this corresponds to spheres with diameters in the ranges 0.65 to $0.7\overline{\sigma}$ and 1.3 to $1.35\overline{\sigma}$. We also define relaxation times $\tau^{(s)}$ and $\tau^{(l)}$ from $F_s^{(s)}(q, t)$ and $F_s^{(l)}(q, t)$, respectively, using the analogues of Eq. (3). $\tau^{(s)}$ and $\tau^{(l)}$ for $w = 0.7$ are plotted as filled triangles in Fig. 2. The ratio $\tau^{(l)}/\tau^{(s)}$ increases with increasing density but slower than τ does. At $\eta = 0.57$ the ratio is approximately 10.

A feature of the dynamics when τ is large is that they are heterogeneous, some particles travel much farther than others in a time τ. In a fluid of monodisperse particles these heterogeneities are dynamic, a particle may be fast at one time but later on may be slow. For polydisperse particles in addition to this source of heterogeneity there is the spread in diameters which means that some particles, the smaller ones, are on average faster than others over all time scales. In Fig. 6 we can compare the α parameter for $w = 0.3$ and 0.7 at the same volume fraction $\eta = 0.57$. α is larger for the more polydisperse spheres; this is the case despite the fact that the relaxation time for the more polydisperse particles is smaller. The system with $w = 0.7$ and $\eta = 0.57$ is at almost the same compressibility factor as the one with $w = 0.3$ and $\eta = 0.56$ so we see that at constant compressibility factor α increases sharply with polydispersity.

For weakly polydisperse spheres the relaxation times for all sizes of sphere increase together and so if we are at high enough density then τ will be very large and on a timescale much less than τ all spheres will be localised, none or at least very few will have moved more than a small fraction of their diameter. However, if spheres with a wide range of diameters are present then the smallest particles will have a relaxation time scale which is much less than τ. Then over some time scale much less than τ but much larger than the relaxation time scale for the smallest particles not all the spheres will be localised. The smallest spheres will be diffusing. This has been observed in binary mixtures of hard spheres in which the smaller spheres are much smaller than the larger spheres, by Jackson et al.[43] The same effect is seen in crystals of binary mixtures.[44] This is an extreme example of polydispersity making the dynamics even more heterogeneous than they are when the particles are all the same size. Note that polydispersity and the heterogeneous

nature of the dynamics when τ is large have the same effect, they produce a wide spread in speeds/relaxation times of the individual particles. Even for monodisperse particles, for times much less than τ the heterogeneous dynamics mean that some particles have left their cages. However, if we have some particles much smaller than others then the small ones may have a relaxation time not much larger and a diffusion constant[43] not much smaller than at lower densities.

6 Discussion

We have studied the dynamics of dense polydisperse hard spheres using molecular dynamics. The relaxation time τ at a given volume fraction was found to depend on the polydispersity, it decreased as the polydispersity increased. So, the glass transition is pushed to higher volume fractions as the spheres become more polydisperse. This is consistent with the increase in the density of random-close-packing with increasing polydispersity.[33, 34] Although we have found this using molecular dynamics, we expect that experiments on polydisperse colloids would show that as polydispersity increased the kinetic glass transition observed in experiment would move to higher volume fractions.

The relaxation time τ is, to a good approximation, a function only of the compressibility factor Z, changing the polydispersity at fixed Z has no effect on τ. This is despite the fact that a characteristic of the dynamics, such as α, changes a great deal at fixed Z as w increases; compare the $w = 0.3$, $\eta = 0.56$ and $w = 0.7$, $\eta = 0.57$ curves in Fig. 6, which have almost the same Z but very different α's. Apparently, increasing the polydispersity at constant volume fraction reduces the relaxation time by reducing Z. The virial equation,[45]

$$Z = 1 - \frac{1}{6NkT}\langle\sum_{i \neq j} \mathbf{r}_{ij}.\mathbf{f}_{ij}\rangle \tag{8}$$

relates Z to the forces between the particles. $\langle\rangle$ denotes an ensemble average. In Eq. (8) $\mathbf{r}_{ij}$ and $\mathbf{f}_{ij}$ are the vector between the centres of the ith and jth particles and the force on the ith particle due to the jth particle, respectively. The sum is over all pairs of particles. So, Z is a constant, 1, plus a term proportional to the sum over the product of the interparticle forces and the interparticle separations. Why the relaxation time should be a function only of this product is not clear to the author.

Although Z can be expressed in terms of forces it is also of course a thermodynamic quantity. At constant temperature Z varies as p/ρ so τ being a function of Z is equivalent to it being a function of the ratio of the pressure to the number density. As the energy of hard spheres is purely kinetic it is independent of volume, thus the pressure is simply the volume derivative of the entropy times the temperature. So, the relaxation time is a function only of Z and so is a function only of the ratio of volume derivative of the entropy to the number density. But it is not a simple

function of it; τ does not vary as the exponential of the Z, it increases more rapidly. The pressure shows no sign of a discontinuity in slope so we conclude that there is no phase transition in the density range studied here. It is an open question whether or not there is a phase transition to an 'ideal' glass phase at higher densities, as assumed by Speedy,[4] see also Refs. 1, 3.

We have characterised the dynamics using the non-Gaussian parameter α, Fig. 6, and the distribution of relaxation times $P(\zeta)$, Fig. 7. The results for α have been compared to experimental results for colloidal suspensions.[5–7] The dynamics are heterogeneous[10–13] by which we mean that there is a broad distribution of speeds and of relaxation times of the particles. This is true not only at times of order the relaxation time τ but also, at higher density and hence τ, for times at least an order of magnitude larger, see Fig. 7. Indeed given the very wide spread of individual relaxation times ζ it is clear that the overall relaxation time τ is inadequate to characterise the time dependence of the dynamics. In particular, relaxation is far from complete even at times much longer than τ. Comparison of our non-Gaussian parameter with that obtained in experiments on colloidal hard spheres showed significant differences. One possible explanation of this is that hydrodynamic interactions between colloidal particles are acting to make the relaxation more cooperative, i.e., acting to increase the clustering shown in Fig. 4. It is known that hydrodynamic interactions tend to favour collective over relative motion.[40]

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Figure 1: The reduced pressure of polydisperse hard spheres. The solid, dashed and dotted curves are the predictions of the BMCSL theory for polydispersity widths of $w = 0.3$, 0.5 and 0.7, respectively. The circles, squares and triangles are the results of simulation, for polydispersity widths of $w = 0.3$, 0.5 and 0.7, respectively.
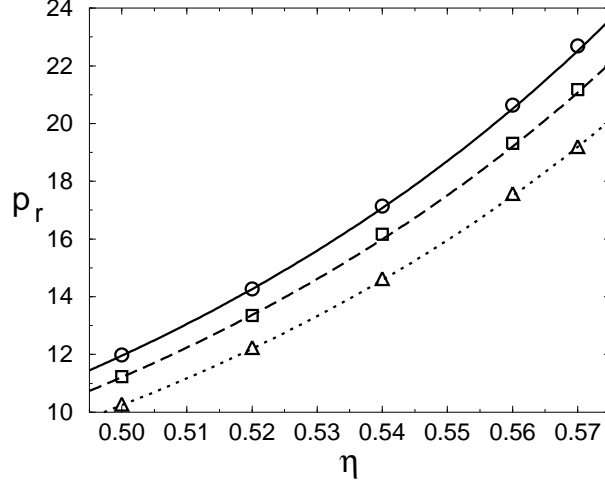

Figure 2: The reduced relaxation time τ as a function of volume fraction η. The open circles, squares and triangles are the results of simulation, for polydispersity widths of $w = 0.3$, 0.5 and 0.7, respectively. The filled triangles are $\tau^{(s)}$ and $\tau^{(b}$, the relaxation times of the the smallest and largest spheres, at a width of $w = 0.7$. The smallest spheres have the smaller τ at all densities.
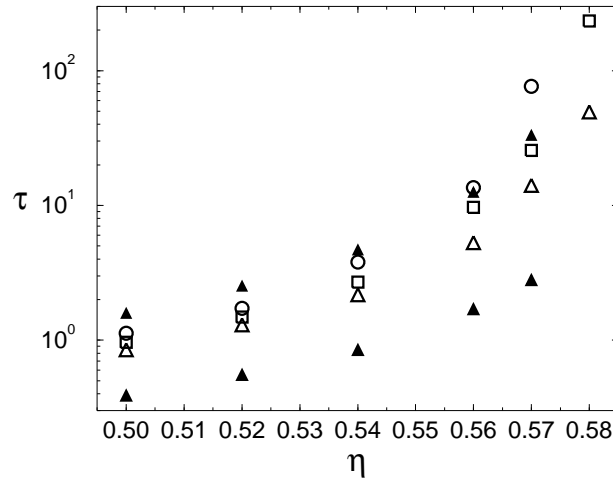
Figure 3: The reduced relaxation time τ as a function of the reduced pressure Z. The circles, squares and triangles are the results of simulation, for polydispersity widths of $w = 0.3$, 0.5 and 0.7, respectively. The +'s are for monodisperse spheres. For $w = 0.3$ and 0.7, and for monodisperse spheres we have extended the calculations down to $\eta = 0.3$.
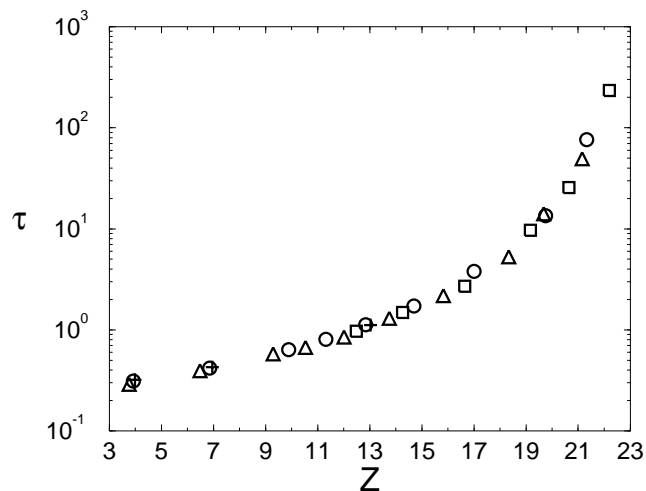

Figure 4: The fastest 5% of our particles, 69 out 1372, are drawn as spheres of diameter $\overline{\sigma}$ (all the spheres are drawn the same size). Fastest is defined as having traveled the largest distance within a time interval of 29.4. The volume fraction $\eta = 0.57$ and $w = 0.3$.
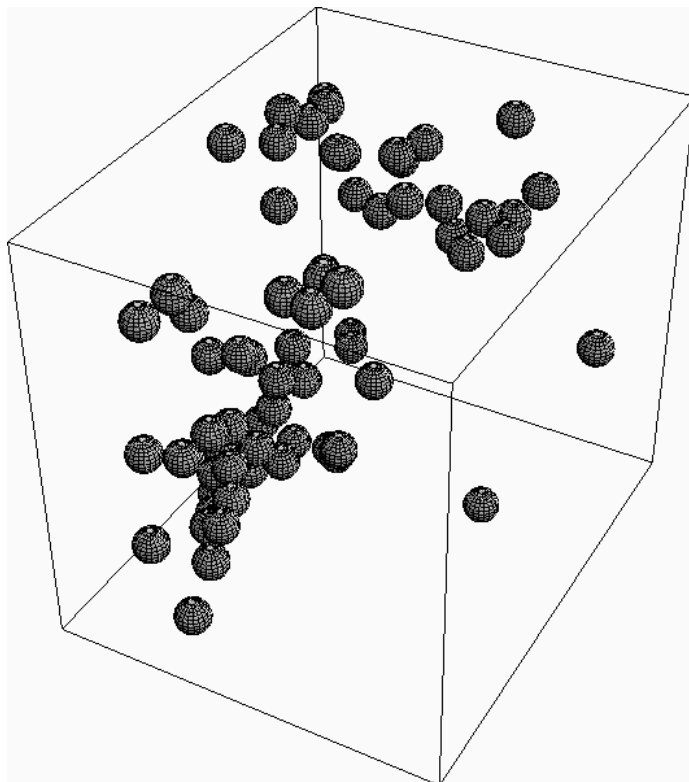
Figure 5: The slowest 5% of our particles, 69 out 1372, are drawn as spheres of diameter $\overline{\sigma}$. Slowest is defined as having traveled the smallest distance within a time interval of 29.4. The volume fraction $\eta = 0.57$ and $w = 0.3$.
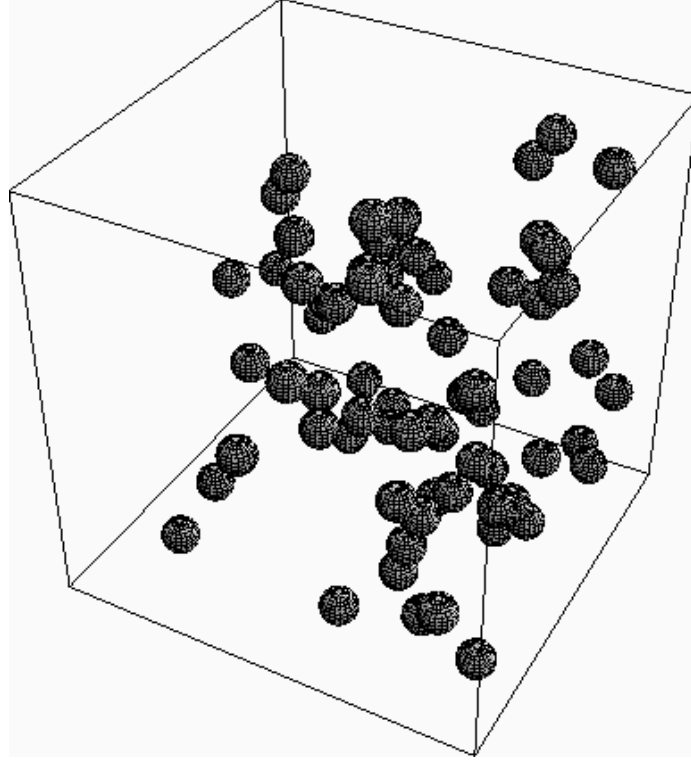

Figure 6: The non-Gaussian parameter α as a function of time. The circles and squares are for a polydispersity widths $w = 0.3$ and 0.7, respectively. The three curves for $w = 0.3$ are from bottom to top, for $\eta = 0.52$, 0.56 and 0.57. The squares are for $\eta = 0.57$.
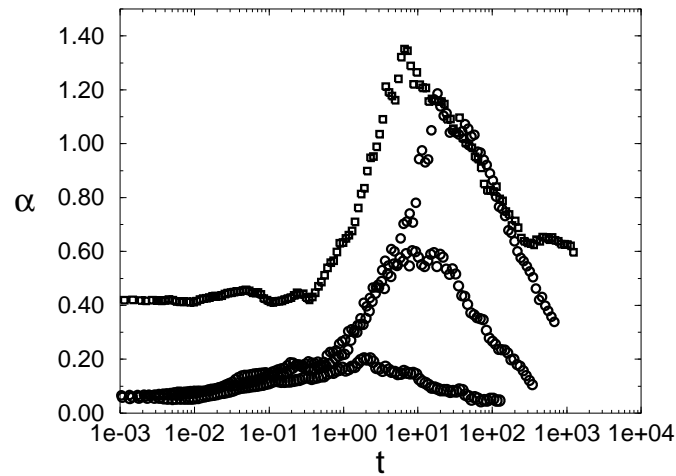
Figure 7: The probability distribution function for relaxation times of individual particles. The crosses and squares are for $\eta = 0.5$ and 0.56, respectively; $w = 0.3$.